

# Maximum-valence radii of transition metals

(covalent radii/enneacovalence)

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Contributed by Linus Pauling, July 16, 1975

**ABSTRACT** In many of their compounds the transition metals have covalence 9, forming nine bonds with use of nine hybrid *spd* bond orbitals. A set of maximum-valence single-bond radii is formulated for use in these compounds. These radii are in reasonably good agreement with observed bond lengths. Quadruple bonds between two transition metal atoms are about 50 pm (iron-group atoms) or 55 pm (palladium and platinum-group atoms) shorter than single bonds. This amount of shortening corresponds to four bent single bonds with the best set of bond angles, 79.24° and 128.8°.

The magnetic properties of the iron-group transition metals indicate (1) that the valence of these metals is 6 (from chromium to nickel) or less, and a set of single-bond metallic radii corresponding to these values of the valence has been formulated (2). Although nine hybrid orbitals can be formed from the 3*d*, 4*s*, and 4*p* orbitals, the calculations made by Hultgren (3) for cylindrically symmetrical bond orbitals seemed to indicate that only six were well suited to bond formation. By abandoning the restriction to cylindrical symmetry of the bond orbitals McClure (4) has recently shown that in fact nine good *spd* bond orbitals can be formed, with strengths 2.9539 to 2.9936, close to the maximum value, 3. I have now found that the structures of many compounds of transition metals can be discussed in a satisfying way on the basis of covalence 9 (or 8 in some cases) and have formulated a corresponding set of maximum-valence single-bond radii, given in Table 1. These radii may be used in interpreting the experimental values of bond lengths.

It was recognized long ago that the formulas of the carbonyls Cr(CO)<sub>6</sub>, Fe(CO)<sub>5</sub>, and Ni(CO)<sub>4</sub> correspond to completion of the argon structure (9 outer electron pairs, shared or unshared) by the metal atom. In Ni(CO)<sub>4</sub>, for example, the nickel atom might form *sp*<sup>3</sup> single bonds (a shared electron pair) with each of the four carbon atoms and have five unshared pairs in its 3*d* orbitals. This structure is not acceptable, however, because it gives the nickel atom the formal charge -4, which cannot be overcome by the partial ionic character of the bonds. The structure in which the nickel atom has one unshared pair and forms double bonds with each of the carbon atoms, giving nickel the covalence 8 and zero formal charge, was suggested in 1921 by Langmuir (5) and verified in 1935 by the determination of the nickel-carbon bond length as 182 ± 3 pm by Brockway and Cross (6). In Fe(CO)<sub>5</sub> we assign double bonds from the iron atom to four carbon atoms and a single bond (with transfer of an electron to the iron atom) to the fifth, and in Cr(CO)<sub>6</sub> three double bonds and three single bonds to carbon atoms, giving valence 9 to iron and chromium. The amount of ionic character of the metal-carbon bonds is large enough to make these structures compatible with the electroneutrality principle.

The structure for Co<sub>2</sub>(CO)<sub>8</sub> with cobalt-carbon double bonds and a cobalt-cobalt single bond corresponds to valence 9 and the argon structure for cobalt. The observed cobalt-

cobalt bond length 252.4 ± 0.2 pm (7) leads directly to 126.2 pm for the single-bond covalent radius for cobalt with valence 9. Similar values are reported for *R*<sub>1</sub> (*v* = 9) in other molecules with cobalt-cobalt bonds: 123.5 pm in dicobalt-hexacarbonyl diphenylacetylene (8), 123.5 pm in ethylidene tri(cobalttricarbonyl) (9), 123.5 pm in bis(tricobalt-enneacarbonyl)acetone (10), 122.4 to 124.3 pm in Co<sub>5</sub>(CO)<sub>15</sub>C<sub>3</sub>H (11), and 124.4 pm in hexacarbonyl-3,4,5,5,6,6-hexafluorocyclohexa-1-yne-3-enedicobalt (12). Values of *R*<sub>1</sub> (*v* = 9) for iron are given by observed iron-iron bond lengths as, for example, 123 pm in Fe<sub>2</sub>(CO)<sub>9</sub> (13), 132 pm in Fe<sub>5</sub>(CO)<sub>15</sub>C (14), 123.4 pm in Fe<sub>3</sub>(C-O)<sub>8</sub>(C<sub>6</sub>H<sub>5</sub>CCC<sub>6</sub>H<sub>5</sub>)<sub>2</sub> (15), and 126.4 pm in 1,5-di(irontricarbonyl)-3-methylenepenta-1,4-diene (16). From these values and many others I have composed a set of values of maximum-valence (*v* = 9) single-bond radii for the transition metals. These values, given in Table 1, are from 8 to 12 pm larger than the single-bond metallic radii, which for these metals correspond to the valence 6.

The following equation (17) is to be used in calculating the bond length for a bond with bond number *n* (less than 1) between atoms A and B:

$$\text{Bond length} = R_1(A) + R_1(B) - 60 \text{ pm} \log n - c|x_A - x_B| \quad [1]$$

In this equation *x*<sub>A</sub> is the electronegativity of atom A and *c* is the Schomaker-Stevenson factor, with value 8 pm for bonds to first-row elements (C, N, O, F), and 6, 4, and 2 pm, respectively, for bonds to more electronegative second-row, third-row, and fourth-row elements (ref. 17, p. 229). Values of *R*<sub>1</sub> are 77.2 pm for C, 74 pm for N, and 74 pm for O. A correction of -2 pm in the radius of carbon for bonds adjacent to a double bond is to be made (ref. 17, p. 233).

An example is Os<sub>4</sub>O<sub>4</sub>(CO)<sub>12</sub> (18). The four Os and four O atoms lie at the alternating corners of a distorted cube, with edge (Os—O bond length) 206 ± 2 pm, and each osmium atom has 3 CO attached, with Os—C bond length 191.5 ± 4 pm. Each oxygen atom becomes tercovalent by transferring an electron to an osmium atom, giving it 9 outer electrons, which with the 9 *dsp* bond orbitals permit it to form three single bonds (*n* = 1) to the adjacent oxygen atoms and three double bonds (*n* = 2) to the carbon atoms. From Eq. 1, with *x* = 2.2 for Os, 3.5 for O, and 2.5 for C (17), we calculate bond lengths Os—O = 202 pm and Os=C = 190 pm, in agreement with experiment. (The double bond is taken to be 21 pm shorter than the corresponding single bond, as is found for carbon-carbon bonds.)

Another example, one of many that might be given, is the violet iron carbonyl diphenylacetylene complex Fe<sub>3</sub>(C-O)<sub>8</sub>(C<sub>6</sub>H<sub>5</sub>C<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> (15). Each iron atom achieves the valence 9 by receiving an electron from one carbonyl group, with which it forms a single bond (Fe<sup>-</sup>—O≡C:). One iron atom also forms a double bond with a second carbonyl group

Table 1. Single-bond radii for transition metals with covalence 9 (in pm)

Cr	Mn	Fe	Co	Ni
126	125	124	123	122
Mo	Tc	Ru	Rh	Pd
139	138	137	136	135
W	Re	Os	Ir	Pt
140	139	138	137	136

(Fe=C=O:), two single bonds with iron atoms (in an Fe<sub>3</sub> ring), and four bonds with acetylenic carbon atoms, and each of the other iron atoms forms a single bond and two double bonds with carbonyl groups, two single bonds with iron atoms, and two single bonds with carbon atoms. The calculated Fe—Fe bond length, 248 pm, lies between the observed values, 246 and 259, average 251 pm. The calculated Fe—C single-bond value, 196 pm, is slightly smaller than the observed value, 200 ± 2 pm, and the calculated Fe—C (carbonyl) double-bond value, 178 pm, agrees with the observed value, 176 ± 3 pm. The calculated value includes a correction 5 pm to the pure double-bond value for the 37.5% average single-bond character contributed by one Fe<sup>2+</sup>—C≡O: per iron atom (ref. 17, p. 239).

Another example is (CO)<sub>3</sub>Cr(AsCH<sub>3</sub>)<sub>3</sub>Cr(CO)<sub>3</sub> (19). The nine arsenic atoms form a nine-membered ring, with three bonded to each of the chromium atoms, bond length 244 ± 1 pm, in good agreement with the value 242 pm calculated with use of the tetrahedral radius 118 pm for arsenic. The observed chromium-carbon distance is 177 ± 4 pm, in agreement with the calculated double-bond distance 173 pm.

### Bonds to phosphine and arsine

Phosphine and arsine and their derivatives may function in the same way as carbon monoxide to transfer an electron to a transition-metal atom, by forming a single bond, such as Fe<sup>2+</sup>—P<sup>+</sup>R<sub>3</sub>. The length of such a bond would be calculated with use of the tetrahedral R<sub>1</sub> for phosphorus, 110 pm, or arsenic, 118 pm. A double bond, M=PR<sub>3</sub> or M=AsR<sub>3</sub>, may also be formed, giving P or As a transargononic structure, which corresponds to values of R<sub>1</sub> about 10 pm larger. For example, in the molecule RhH[P(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>] (20) the rhodium atom forms a single bond with the hydrogen atom and a double bond with each of the four phosphorus atoms. The length of the Rh=P bond calculated with the transargononic radius 120 pm for phosphorus is 237 pm, in agreement with the observed value 238 pm.

### Multiple bonds

A strikingly short rhenium-rhenium bond, 222 pm long, was reported in 1963 by Kuznetsov and Koz'min (21), and it was soon recognized as a quadruple bond by Cotton. During the last dozen years quadruple bonds have been reported in many crystals. A summary of structures and bond lengths has been published by Cotton (22).

Four of the nine hybrid *dsp* bond orbitals may be involved in forming four bent single bonds, constituting a quadruple bond. It has been recognized that the picture of a double bond or triple bond between carbon atoms as involving bent single bonds explains the bond lengths C=C = 133 pm and C≡C = 121 pm; two or three circular arcs with length 154 pm, the single-bond value, and starting and ending at the tetrahedral angle 109.47° have chords 132 pm and

118 pm, rather close to the observed values. We may use a similar argument to calculate the expected length of a quadruple bond from that for a single bond. The best *spd* bonds are formed at the angles 73.15° and 133.62° (ref. 17, p. 152). There is a relation between the angles between pairs of four vectors related by the operations of a 4-fold symmetry axis such that with four angles 73.15° the other two equal 114.85°, and if these two equal 133.62°, the other four equal 81.08°. The best solution, minimizing the sum of the squares of the deviations from the best angles, is that with four angles 79.24° and two angles 128.8°. This best solution leads to a chord less than the arcs by 19.77%. From Table 1 we accordingly predict bond length 202 pm for Cr≡Cr (shortening 50 pm), 223 pm for Re≡Re (shortening 55 pm), and similar values for other quadruple bonds.

The observed Cr≡Cr bond lengths (22) in Mg<sub>2</sub>Cr<sub>2</sub>(CO)<sub>4</sub>·6H<sub>2</sub>O, Li<sub>4</sub>Cr<sub>2</sub>(C<sub>4</sub>H<sub>8</sub>)<sub>4</sub>·4tetrahydrofuran, Li<sub>4</sub>Cr<sub>2</sub>(CH<sub>3</sub>)<sub>8</sub>·4tetrahydrofuran, and Cr<sub>2</sub>(allyl)<sub>4</sub> are 2.22, 197.5, 198, and 197 pm, respectively (22). Except for the first, these values agree well with the calculated value 198 pm. This value is calculated with use of R<sub>1</sub> (v = 8) = 123.5 pm for Cr, obtained by interpolation between R<sub>1</sub> (9) = 126 pm (Table 1) and R<sub>1</sub> (6) = 118.6 pm (ref. 17, p. 403), and the quadruple-bond correction -19.77%; the substances all involve chromium atoms with eight valence electrons. For Re≡Re the average of seven experimental values quoted by Cotton (22) for molecules in which rhenium is enneacovalent, such as (C<sub>6</sub>H<sub>5</sub>N)<sub>2</sub>Re<sub>2</sub>Cl<sub>8</sub>, is 222.9 pm (range 221.3 to 224.4), in agreement with the calculated value 223 pm. For molecules in which rhenium is octacovalent the value 218 pm is calculated; observed values (22) for such molecules are 219.8 for Re<sub>2</sub>I<sub>4</sub>(O<sub>2</sub>CC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, 222.2 for Re<sub>2</sub>Cl<sub>6</sub>[P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>, and 221.3 for Cs<sub>2</sub>Re<sub>2</sub>Br<sub>8</sub>.

For Mo≡Mo observed bond lengths (22) in molecules in which the molybdenum atoms are bonded to carbon or sulfur atoms (electronegativity 2.5) are 218.3 pm [in Mo<sub>2</sub>(allyl)<sub>4</sub>], 214.7 pm [in Mo<sub>2</sub>(CH<sub>3</sub>)<sub>8</sub>4<sup>-</sup>], and 212.5 pm [in Mo<sub>2</sub>(S<sub>2</sub>COC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>·2tetrahydrofuran], whereas in molecules in which they are bonded to more electronegative atoms they are 214.1 pm (average for three molecules with Mo—Cl bonds), 209.0 pm (in one molecule with Mo—N bonds), and 210.6 pm (average for four molecules with Mo—O bonds). These values, except for the first one, agree only roughly with the value 218 calculated with the value 136 pm for the octacovalent radius of molybdenum.

In general, the observed lengths of quadruple bonds support the bent-bond calculation of shortening by about 20 percent, which is about 50 pm for metals of the iron group and 55 pm for those of the palladium and platinum groups. The bent-bond calculation for *spd* orbitals at the best bond angle 73.15° gives shortening by 6.7% for a double bond and by 9.3% for a triple bond. The calculated Fe=Fe distance, 232 pm, agrees with one of the three values quoted by Cotton (22) 232.6 pm for (ON)<sub>2</sub>Fe<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>, but not with the other two, 221.5 and 222.5 pm. For Re=Re the calculated value 259 pm is a little larger than the experimental values 255 pm for (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Re<sub>2</sub>[C(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub> and 246 pm for (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Re<sub>2</sub>(CO)[C(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]. The nine *spd* orbitals form a complex system, and the direction and nature of the other bonds formed by a transition metal atom may affect the double and triple bonds in such a way as to change their length.

This work was supported in part by a grant from The Educational Foundation of America, 35 Church Lane, Westport, Conn. 06880.

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